

平成16年登録第

認

証



Kazuyuki MATSUOKA et al.
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BIRCH, STEWART, KOLASCH: BIRCH, LLP

嘱託人三宅有紀は、本公証人の面前で、別添文書に署名した。(703)205-8000



よって、これを認証する。

平成16年 5 月 12 日、本公証人役場において
東京都千代田区内幸町2丁目1番1号
東京法務局所属

公証人
Notary

藤井 一
TOICHI FUJIWARA



証 明

上記署名は、東京法務局所属公証人の署名に相違ないものであり、かつ、その押印は、
真実のものであることを証明する。

平成16年 5 月 12 日

東京法務局長

石井政治



APOSTILLE

(Convention de La Haye du 5 octobre 1961)

1. Country: JAPAN

This public document

2. has been signed by **TOICHI FUJIWARA**

3. acting in the capacity of Notary of the Tokyo Legal Affairs Bureau

4. bears the seal/stamp of **TOICHI FUJIWARA**

Certified

5. at Tokyo

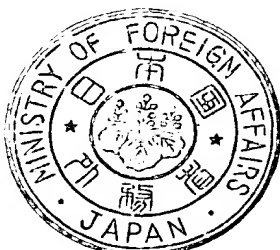
6. MAY 12 2004

7. by the Ministry of Foreign Affairs

8. 04- N° 002445

9. Seal/stamp:

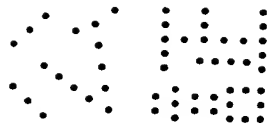
10. Signature



S. Hagiwara

Shinichi HAGIWARA

For the Minister for Foreign Affairs



Registration No. 714

DECLARATION

I, Yuki MIYAKE residing at 1223-1 A-409, Sonno-cho, Inage-ku, Chiba-shi, Chiba, 263-0051, Japan do hereby solemnly and sincerely declare:

1. That I am an employee of Furuya & Co. located
at Hamacho-Hanacho Building, 2-17-8, Nihonbashi-Hamacho, Chuo-ku,
Tokyo 103-0007, Japan,
2. That I am well acquainted with the Japanese and English
languages, and
10. That the attached English document is a true and correct translation into
English of the certified copy of the Japanese patent application No. 6-
318548 filed on 21 December 1994, a copy of which is hereto attached.

And I make this solemn declaration conscientiously
believing the same to be true and correct.

on the date of 12 May 2004

三宅 有紀

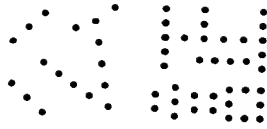
By Yuki MIYAKE

This is to certify that this document
was subscribed before me by the above-named
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MAY 12 2004

TOICHI FUJIWARA
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NOTARY



Patent Office
Japanese Government

This is to certify that the annexed is a true copy of the following application as filed with this office.

Date of Application: 21 December 1994

Application Number: patent application No. 6-318548

Applicant(s): Daicel Chemical Industries, Ltd.

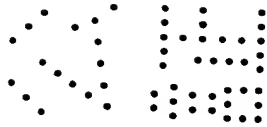
dated 5 January 1996

Commissioner

Patent Office

Mr. Yuji KIIYOKAWA

Shusho No.
Shushotokuhei 07-3078265



[Designation of Document] Patent Application

[Reference Number] 194DK103

[Application Date] 21 December 1994

[Addressee] the Commissioner of the Patent
Office

[IPC] C06D 5/06

[Title of the Invention] Gas Generant Composition

[Number of Claims] 8

[Inventor]
[Address or Residence] 3-4-16 Yoneyamadai
Kanmakicho, Kitakatsuragi-gun,
Nara

[Name] Kazunori MATSUOKA

[Inventor]
[Address or Residence] Kamiyobeminamiapart 5-3,
610-1 Kamiyobe,
Yobe-ku, Himeji-shi, Hyogo

[Name] Shogo TOMIYAMA

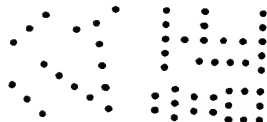
[Applicant]
[Identification Number] 000002901

[Name] Daicel Chemical Industries, Ltd.

[Representative] Akio KOJIMA

[Agent]
[Identification Number] 100063897

[Patent Attorney]
[Name] Kaoru FURUYA



[Telephone Number] 03(3663)7808

[Selected Agent]

[Identification Number] 100076680

[Patent Attorney]

[Name] Takahiko MIZOBE

[Selected Agent]

[Identification Number] 100087642

[Patent Attorney]

[Name] Satoshi FURUYA

[Selected Agent]

[Identification Number] 100091845

[Patent Attorney]

[Name] Shinji MOCHIDA

[Designation of the Payment]

[Way of Payment] prepayment

[Number of the Deposit] 010685

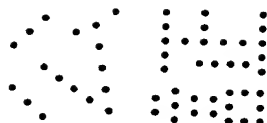
[Amount of the Payment] 21,000

[List of the Exhibit]

| | | |
|-----------------------|---------------|---|
| [Name of the Subject] | Specification | 1 |
| [Name of the Subject] | Abstract | 1 |

[Number of the General Power of Attorney] 9005922

[Request of the proof] yes



JP6-318548

[Designation of Document] Specification

[Title of the Invention] Gas Generant Composition

[Claims]

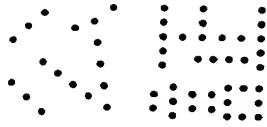
[Claim 1] A gas generant composition having, as the essential components, a nitrogen-containing organic compound and an oxygen-containing inorganic oxidizer, which comprises copper oxide having a specific surface area of not less than $1 \text{ m}^2/\text{g}$.

[Claim 2] The gas generant composition according to claim 1, wherein copper oxide has a specific surface area of not less than $1 \text{ m}^2/\text{g}$ and an average particle size of not more than 5μ .

[Claim 3] The gas generant composition according to claim 1 or 2, wherein the nitrogen-containing organic compound is at least one selected from the group consisting of organic compounds containing amino group or amido group and tetrazole derivatives

[Claim 4] The gas generant composition according to claim 3, wherein the organic compound containing amino group or amido group is azodicarbonamide.

[Claim 5] The gas generant composition according to claim 3, wherein the tetrazole derivative is aminotetrazole.



[Claim 6] The gas generant composition according to claim 1 or 2, wherein the oxygen-containing inorganic oxidizer is at least one selected from the group consisting of KNO_3 , $\text{Sr}(\text{NO}_3)_2$, and KClO_4 .

[Claim 7] The gas generant composition according to claim 1 or 2, wherein the oxygen-containing inorganic oxidizer is KClO_4 .

[Claim 8] The gas generant composition according to claim 1 or 2, wherein the nitrogen-containing organic compound is azodicarbonamide and the oxygen-containing inorganic oxidizer is KClO_4 .

[Detailed Description of the Invention]

[0001]

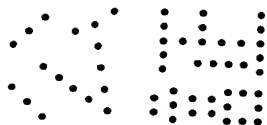
[Field of Industrial Application]

The present invention relates to a gas generant composition. More specifically, the invention relates to a non-azide type gas generator composition which supplies gas components by burning for the purpose of inflating an air bag system.

[0002]

[Prior Art]

In the event of collision of vehicles like cars at high speed, the driver and passengers might be injured or killed

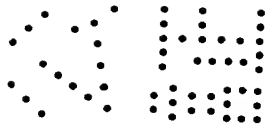


by clashing against internal hard or dangerous parts of the vehicles such as the handle and front glass. In order to prevent such disasters, air bag systems for automobiles have been developed which inflate quickly by a gas generated from a gas generant.

Requirements for the gas generant of an automobile air bag system are very severe. At first, the bag should inflate in a very short period of time, usually not longer than 40 to 50 milliseconds. Further, The atmosphere within the bag is most suitable when it corresponds to the air composition in the car. These requirements are satisfied by gas generants which have been currently used in common comprising a base gas generant such as alkali metal salts (in particular sodium azide) or alkaline earth metal salts of hydrazoic acid. However, these gas generants are seriously defective in that the main component, sodium azide is toxic and that the by-products alkali components are also toxic. Hence, environmental pollution brought by a large amount of scrap cars and health hazard of the driver and passengers when the gas is generated are concerned.

[0003]

For the purpose of overcoming these problems, non-azide type gas generants have been under development in place of sodium azide type. For example, JP-A 3-208878 discloses a

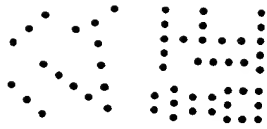


composition which comprises a main component of oxygen-containing oxidizer such as tetrazole, triazole, or their metal salts combined with ammonium perchlorate or sodium nitrate and an auxiliary component of a metal oxide such as V_2O_5 , CuO or Fe_2O_3 . The metal oxide mentioned forms a solid combustion product, which is easily removed by filtration when undesired components are removed by filtration prior to release the formed gas into the bag in an air bag system, and converts CO which is toxic to human bodies generated from the nitrogen-containing organic compound to CO_2 . JP-B 64-6156 and JP-B 64-6157 disclose a gas generant which contains, as the main component, a metal salt of bitetrazole compound that does not contain hydrogen. JP-A 3-208878 further discloses a gas generant having a transition metal complex of aminoarazole as the main component. These non-azide type compounds disclosed in the series of prior art references are characteristic in that the concentration of carbon monoxide released is low since the carbon number in the one molecule is small; however, the performance is not satisfactory in respect of the inflation period of the bag.

[0004]

[Problem to be Solved by the Invention]

The present inventors previously had found that a



non-azide type gas generant having a nitrogen-containing organic compound such as azodicarbonamide and a certain inorganic oxygen-containing oxidizer as the effective component is free from environmental pollution, satisfactory in respect of the inflation period of the bag, and advantageous in the cost, and filed the patent applications (with reference of JP-A 4-185251, JP-A 4-185253 and JP-A 5-18782) .

[0005]

In the combustion of an organic compound containing oxygen, it is well-known that carbon monoxide will generate as incomplete combustion product even when an oxidizer is used in an amount exceeding the chemical equivalence that releases the necessary amount of oxygen for burning combustible elements, such as carbon, hydrogen and others, in the organic compound. In view of this fact, the nitrogen compound, such as azodicarbonamide, used as the main agent in the mentioned gas generant is supposed to release a relatively rather large amount of carbon monoxide and nitrogen oxides since many carbon atoms are contained per molecule. For the purpose of avoiding such by-product carbon monoxide, use of a catalyst may be possible which convert carbon monoxide to carbon dioxide. Many components are known for such catalysts as written in a book "Classified

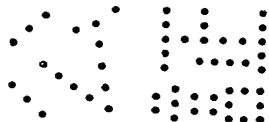


Table for Catalysts depending on Reaction, Vol. I" edited by Tarama et al. of Kyoto University and published by Kagaku Kogyo-sha (see pp. 291-292). However, no catalysts are known that are generally reactive enough in a contact period of time of several dozens milliseconds as required for a gas generant for air bag system; V_2O_5 , CuO , Fe_2O_3 and other metal oxides are used at present in spite of their low activity.

[0006]

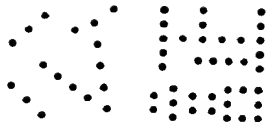
[Means to Solve the Problem]

The present inventors made every effort to solve the above problem, and they finally have found that the property of copper oxide, which is in the above prior art, exhibits an important function for oxidation, thereby completing the present invention.

In other words, the present invention provides a gas generant composition having a nitrogen-containing organic compound and an oxygen-containing inorganic oxidizer as the essential components, in which the composition is characterized by comprising copper oxide having a specific surface area of not less than $1 \text{ m}^2/\text{g}$.

[0007]

The gas generant composition of the present invention contains a nitrogen-containing organic compound and a

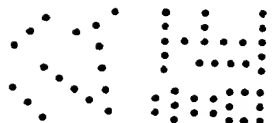


oxygen-containing inorganic oxidizer as the essential components.

There is no particular limitation for the nitrogen-containing organic compound usable for the present invention provided that nitrogen atom is contained in the molecule; examples of the nitrogen-containing organic compound include organic compounds containing amino group or amido group and tetrazole derivatives. Specific examples of the organic compounds containing amino group or amido group include: azodicarbonamide, urea, aminoguanidine bicarbonate, biuret, dicyandiamide, and hydrazides; preferably azodicarbonamide. Specific examples of the tetrazole derivatives include: aminotetrazole, tetrazole, azotetrazole, bitetrazole, tetrazole carboxylate, their alkali metal salts and their alkaline earth metal salts; and preferably aminotetrazole. The nitrogen-containing organic compound may be used in single or as a mixture of two or more kinds.

[0008]

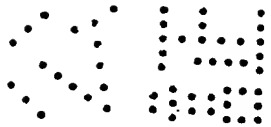
The oxygen-containing inorganic oxidizer usable in the present invention may be selected widely from known ones such as nitrates, nitrites, and oxyhalogenates. Specific examples of the oxygen-containing inorganic oxidizer include potassium nitrate, sodium nitrate, strontium



nitrate, potassium nitrite, sodium nitrite, sodium perchlorate, potassium perchlorate, sodium chlorate, and potassium chlorate. More specifically, a single compound or mixture selected from KNO_3 , $\text{Sr}(\text{NO}_3)_2$ and KClO_4 may be used; KClO_4 is preferable in particular.

[0009]

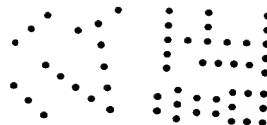
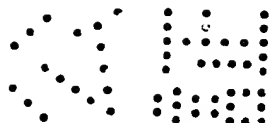
The blend ratio of the nitrogen-containing organic compound to oxygen-containing inorganic oxidizer in the gas generant composition of the present invention may be optionally selected depending on the combustion rate, combustion temperature and combustion temperature, although the ratio is normally selected so as to be stoichiometric when the nitrogen-containing organic compound is completely oxidized and burned on the basis of the oxygen amount. For example, about 20 through 400 parts by weight of the oxygen-containing inorganic oxidizer is blended with 100 parts by weight of the nitrogen-containing organic compound; blending some excess amount of the oxygen-containing inorganic oxidizer compared to the stoichiometric amount for complete combustion is preferred for enhancing the efficiency of oxidizer catalyst provided that the gas generation efficiency based on the unit weight of the gas generant composition is not substantially lowered.



[0010]

According to the present invention, in a gas generant composition containing a nitrogen-containing organic compound and an oxygen-containing inorganic oxidizer as the essential components, copper oxide having a specific surface area not less than $1 \text{ m}^2/\text{g}$, preferably $1.5\text{-}100 \text{ m}^2/\text{g}$, is further blended as the oxidation catalyst. Use of copper oxide of specific surface area less than $1 \text{ m}^2/\text{g}$ does not bring the effect of decreasing carbon monoxide in the generated gas.

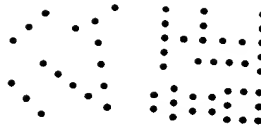
The copper oxide can be produced by a process known to the art. For example, aqueous solution of caustic soda or ammonia is added to aqueous solution of copper chloride to yield copper hydroxide, which is turned to copper oxide by baking. The baking is generally preferred to be done near the temperature at which copper hydroxide is decomposed to copper oxide since higher baking temperature will not bring copper oxide having a large surface area; specifically, practical baking temperature is from 200 to 500°C . Copper oxide is also produced by addition of an alkali carbonate solution to a divalent copper salt solution to prepare basic copper carbonate, followed by baking. Further, copper oxide is also produced by electrolysis of aqueous sodium chloride using copper plates for both electrodes to produce



cuprous oxide, which is baked to turn into copper oxide. Copper oxide produced by various processes as mentioned is crushed by an atomizer, ball mill or other device; thereby, the copper oxide used in the present invention is obtained. However, any copper oxide having a specific surface area not less than $1 \text{ m}^2/\text{g}$ is acceptable and its production process is not limited. The particle size of copper oxide is not limited specifically as well; however, generally 5 μm or less is preferable and the range from 0.5 through 5 μm is more preferable. Exceed 5 μm is not preferable because of low activity and fine powder such as 0.5 μm or less is not preferable because of excessive load for the filter in filtration step.

[0011]

In the present invention, the content of copper oxide is not limited, but normally 1 through 40% by weight, preferably 3 through 30% by weight, and more preferably 3 through 25% by weight, of the total weight of the composition that includes the gas generant containing the nitrogen-containing organic compound and oxygen-containing inorganic oxidizer as the essential components and further a blended third component. Too much copper oxide content is not desirable because the amount of generated gas is decreased against unit weight of the gas generant



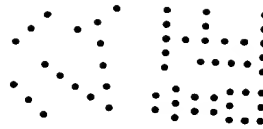
composition; and too little content is not desirable because the effect of decreasing toxic gas concentration is unsatisfactory.

[0012]

For the purpose of enhancing the shaped strength of the gas generant composition, a binder, a decomposition promoter of nitrogen-containing organic compound, silica or the like may be blended. Examples of the binder include: fine crystal binders such as marketed under the trade name "Avicel"; polymer binders such as poval; organic binders such as starch. As a decomposition promoter of nitrogen-containing organic compound, an oxide decomposition promoter or an organic decomposition promoter can be used. Examples of an oxide decomposition promoter are, specifically, ZnO , ZnCO_3 , MnO_2 , FeCl_3 , Pd_3O_4 , PdO_2 , PdO , Sb_2O_3 , TiO_2 , V_2O_5 , CeO_2 , Ba_2O_3 , CaO_2 , YbO_3 , and the like.

[0013]

The composition according to the present invention is prepared by blending respective components mentioned above; resulting blended composition may be used as such for a gas generant, however, a formulated form is preferable. Any known methods are applicable for the formulation, and a suitable binder may be selected. Shape of the formulated composition is not limited specifically and may be, for



example, pellet, disc, ball, like-confetti, and like-tetrapod. The formulated composition may be without holes or with holes (such as briquette with holes or ring shape).

[0014]

[Effect of the Invention]

According to the present invention, in a gas generant composition containing a nitrogen-containing organic compound and an oxygen-containing inorganic oxidizer as the essential components, toxic components in the released gas, in particular carbon monoxide, can be reduced to a practical level which is acceptable as an air bag system for automobile.

[0015]

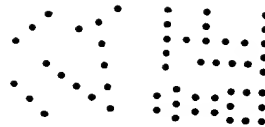
[Examples]

Now, the present invention is explained more specifically concerning the first to fifth embodiments by way of examples; however, the present invention is not limited to these examples if not out of the scope and spirit of the invention.

Hereinafter, "parts" and "%" are based on weight unless otherwise specified.

[0016]

Example 1

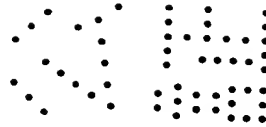


Ten parts of Copper Oxide uF (specific surface area - $4.99 \text{ m}^2/\text{g}$ (by nitrogen adsorption method), average particle size - 1.06μ) marketed by NIKKO FINE PRODUCTS CO., LTD., 45 parts of azodicarbonamide, and 55 parts of potassium perchlorate, 10 parts of copper oxide were blended; furthermore, 5% aqueous solution of a soluble starch is added therewith so that the starch content be 0.55 parts. Resulting humid fine particles were adjusted to suitable fineness and water content for shape formulation, and formed into pellets ($9.7 \text{ mm}\phi \times 4 \text{ mm}\phi$). The pellets were subjected to a predetermined tank test (as described in JP-B 52-3620 and JP-B 64-6156) using a burning device equipped with a filter and coolant; thereby, the concentration of carbon monoxide in the gas generated in the tank was evaluated. The burning pressure and period were of desired values. The concentration of carbon monoxide in the gas generated in the tank was determined to be 0.3% by gas chromatography.

[0017]

Example 2

Example 1 was repeated except that Copper Oxide F (specific surface area - $1.68 \text{ m}^2/\text{g}$ (by nitrogen adsorption method), average particle size - 2.09μ) marketed by NIKKO FINE PRODUCTS CO., LTD., was used as the copper oxide to evaluate the concentration of carbon monoxide in the gas



generated in the tank. The burning pressure and period were of desired values. The concentration of carbon monoxide in the gas generated in the tank was determined to be 1.3% by gas chromatography.

[0018]

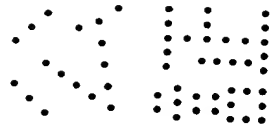
Example 3

Example 1 was repeated except that Copper Oxide (specific surface area - $10.16 \text{ m}^2/\text{g}$ (by nitrogen adsorption method), average particle size - 8.46μ) marketed by NAKARAITESK was used as the copper oxide to evaluate the concentration of carbon monoxide in the gas generated in the tank. The burning pressure and period were of desired values. The concentration of carbon monoxide in the gas generated in the tank was determined to be 2.3% by gas chromatography.

[0019]

Comparative Example 1

The copper oxide used in Example 3, marketed by NAKARAITESQUE, INC., was baked at 800°C under air flow and pulverized thereafter; thereby, a copper oxide catalyst was prepared having a specific surface area of $0.31 \text{ m}^2/\text{g}$. Example 1 was repeated except that the copper oxide used was the copper oxide catalyst thus prepared to evaluate the concentration of carbon monoxide in the gas generated in

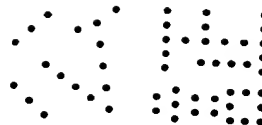


the tank. The burning pressure and period were of desired values. The concentration of carbon monoxide in the gas generated in the tank was determined to be 3.1% by gas chromatography.

[0020]

Example 4

Example 1 was repeated except that N-300 (specific surface area - $1.26 \text{ m}^2/\text{g}$ (by nitrogen adsorption method), average particle size - 1.98μ) marketed by NISSIN CHEMCO was used as the copper oxide to evaluate the concentration of carbon monoxide in the gas generated in the tank. The burning pressure and period were of desired values. The concentration of carbon monoxide in the gas generated in the tank was determined to be 2.4% by gas chromatography.



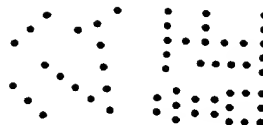
[Designation of Document] Abstract

[Abstract]

[Object] To provide a gas generant composition which decreases toxic components, in particular carbon monoxide and nitrogen oxides, in generated gas to a concentration practical as an air bag system for automobile.

[Structure] In the gas generant composition, a nitrogen-containing organic compound such as a compound containing amino group or amido group or a tetrazole derivative and a oxygen-containing inorganic oxidizer such as KNO_3 , $\text{Sr}(\text{NO}_3)_2$ or KClO_4 are essential components. And further, copper oxide having a specific surface area of not less than $1 \text{ m}^2/\text{g}$ is included.

[Selected Drawing] none



[Designation of the Document] Correction Data by Authority

[Corrected Document]

Patent Application

(Recognized and added Information)

[Applicant]

[Identification Number] 000002901

[Address or Residence] 1, Teppō-cho, Sakai-shi,
Osaka

[Name] Daicel Chemical Industries, Ltd.

[Agent] Applicant

[Identification Number] 100063897

[Address or Residence] Furuya & Co.,
Nihonbashi TM Building,
1-8-11, Nihonbashi-Horidomecho,
Chuo-ku, Tokyo

[Name] Kaoru FURUYA

[Selected Agent]

[Identification Number] 100076680

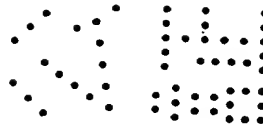
[Address or Residence] Furuya & Co.,
Nihonbashi TM Building,
1-8-11, Nihonbashi-Horidomecho,
Chuo-ku, Tokyo

[Name] Takahiko MIZOBE

[Selected Agent]

[Identification Number] 100087642

[Address or Residence] Furuya & Co.,
Nihonbashi TM Building,
1-8-11, Nihonbashi-Horidomecho,
Chuo-ku, Tokyo



【Name】

Satoshi FURUYA

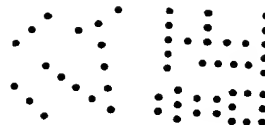
【Selected Agent】

【Identification Number】 100091845

【Address or Residence】 Furuya & Co.,
Nihonbashi TM Building,
1-8-11, Nihonbashi-Horidomecho,
Chuo-ku, Tokyo

【Name】

Shinji MOCHIDA



Particulars of Applicant

| | |
|-----------------------|-----------------------------------|
| Identification Number | [000002901] |
| 1. Date of Changing | August 28, 1990 |
| [Reasons of Changing] | New Registration |
| Address | 1, Teppo-cho, Sakai-shi, Osaka |
| Name | Daicel Chemical Industries, Ltd. |